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(54) CURABLE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a curable composition which gives a cured item which is excellent in clarity and low coloration properties and can retain its clarity and low-coloration properties even after a long-time exposure to high temperatures or after a long-time outdoor exposure.

SOLUTION: This curable composition essentially contains a liquid composition comprising 40-100 wt.% polymerizable monomer component (A) and 0-60 wt.% polymer and/or oligomer component (B). Component A contains, based on its wt., 25-80 wt.% hydroxyl-group-containing (meth)acrylic ester. The curable composition contains, based on 100 pts.wt. above-mentioned liquid composition, 0.1-5 pts.wt. phenolic antioxidant (C), 0.01-5 pts.wt. phosphorus-base antioxidant (D), and 0.5-10 pts.wt. ultraviolet absorber and/or hindered amine light stabilizer (E).

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CLAIMS

[Claim(s)]

[Claim 1]A polymerization nature monomer (A) is 40 to 100 % of the weight, and a polymer and/or oligomer (B) are the hardenability constituents which make indispensable a liquid composition which is 0 to 60 % of the weight. When the whole quantity is made into 100 % of the weight, this polymerization nature monomer (A) is 25 to 80 % of the weight, and acrylic ester which has a hydroxyl group (meta) this hardenability constituent, this -- a liquid composition -- 100 -- a weight section -- receiving -- a phenolic antioxidant -- (- D -) -- 0.01 - five -- a weight section -- and -- an ultraviolet ray absorbent -- and/or -- a hindered amine light stabiliser -- (- E -) -- 0.5 - ten -- a weight section -- containing -- things -- the feature -- carrying out -- hardenability -- a constituent .

[Claim 2]The hardenability constituent according to claim 1 which will be characterized by acrylic ester (meta) being 80 to 100 % of the weight if said polymerization nature monomer (A) makes the whole quantity 100 % of the weight.

[Claim 3]The hardenability constituent according to claim 1 or 2, wherein said polymer and/or oligomer (B) are acrylic polymers which have two or more polymerization nature double bonds in intramolecular (meta).

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001][Field of the Invention]This invention relates to a hardenability constituent. It is related with the hardenability constituent used in more detail suitably for the field expected low coloring at transparency or the time of low coloring especially elevated-temperature exposure, and an outdoor exposure.

[0002][Description of the Prior Art]From the ability of the hardened material which was excellent in hardenability and was excellent in various kinds of physical properties to be formed if a hardenability constituent is a radical hardening type. It is industrially used broadly in fields, such as mold goods, a laminated piece, a cast article, a shock buffer, the elastic buffer of a substrate, a sealing agent, adhesives, encapsulant, an inclusion agent, substrate protection, and a destructive preventing scattering agent of a substrate. In such a field, when a hardened material is formed, it is transparent, and if it can be considered as colorlessness or low coloring, it will become useful for various kinds of uses. It is requested that muddiness and coloring are kept from arising from a viewpoint of raising the endurance of a hardened material when elevated-temperature exposure is carried out over a long period of time, or when extended outdoor exposure is carried out.

[0003]It is indicated that the glass laminate sheet excellent in cold resistance or transparency can be manufactured about the adhesive composition for glass lamination which becomes JP,3-44112,B from the acrylate monomer (meta) of specific structure which has a hydroxyl group, a radical curing catalyst, a silane coupling agent, and a plasticizer. However, so that transparency and low coloring nature can be maintained, when the transparency and low coloring nature at the time of making it harden are improved in this adhesive composition and also elevated-temperature exposure is carried out over a long period of time, or also when extended outdoor exposure is carried out. With the acrylate monomer (meta) of specific structure which has a hydroxyl group, there was room of a device using an antioxidant, an ultraviolet ray absorbent, and/or light stabilizer.

[0004]The polyfunctional monomer which has a hydroxyl group in JP,5-86972,B and has a specific substituent in it, Into polyester acrylates and the acrylate mixture which consists of specific acryloyl stabilizer which has at least one or more sorts of hindered amine structure, and the constituent for coating which consists of adding at least one or more sorts of antioxidants further. However, the polyfunctional monomer in which such a hardenability constituent also has a hydroxyl group and has a specific substituent is polyhydric alcohol. From using polyester acrylates as the essential ingredient, and also the kind or the directions for an antioxidant not being specified. There was room to devise so that transparency and low coloring nature can be maintained, when the transparency and low coloring nature at the time of making it harden are improved and also elevated-temperature exposure is carried out over a long period of time, or also when extended outdoor exposure is carried out.

[0005]

[Problem(s) to be Solved by the Invention]This invention is made in view of the above-mentioned actual condition, and is excellent in transparency or low coloring nature, and an object of this invention is to provide the hardenability constituent which moreover forms the hardened material which can maintain transparency and low coloring nature after elevated-temperature exposure or extended outdoor exposure over a long period of time.

[0006]

[Means for Solving the Problem]A time that this invention persons examine many things about a hardenability constituent which forms a hardened material excellent in transparency or low coloring nature, As opposed to a liquid composition which specified a weight percentage with a polymerization nature monomer (A) and a polymer in which a hardenability constituent carries out specific amount content of the acryloyl ester which has a hydroxyl group (meta), and/or oligomer (B), If specific amount combination of a phenolic antioxidant (C), the Lynn system antioxidant (D) and an ultraviolet ray absorbent, and/or the hindered amine light stabiliser (E) is carried out, It thought out for it to be able to excel in transparency and low coloring nature at a time of making it harden, for transparency and low coloring nature to be maintained over a long period of time moreover, and for an aforementioned problem to be solved splendidly. In such a hardenability constituent, acryloyl ester (meta) has a hydroxyl group, for example, And it is thought that a synergistic effect by having combined two sorts of specific antioxidants, an ultraviolet ray absorbent, and/or a hindered amine light stabiliser will be demonstrated, and it will have the above-mentioned operation effect.

Transparency and low coloring nature have been maintained by choosing a specific curing system. If acryloyl ester (meta) which inside cold cure nature is realizable and can give pliability is used, It also finds that balance of a substrate adhesive property, substrate adhesion, elastic repeatability, and a **** pace of expansion of tensile strength can be made good with transparency or low coloring nature maintained, and this invention is reached.

[0007]Namely, polymerization nature monomer (A) of this invention is 40 to 100 % of the weight, And a polymer and/or oligomer (B) are a liquid composition which is 0 to 60 % of the weight the hardenability constituents made indispensable, and the above-mentioned polymerization nature monomer (A). When the whole quantity is made into 100 % of the weight, acryloyl ester which has a hydroxyl group (meta) is 25 to 80 % of the weight, and the above-mentioned hardenability constituent, the above -- a liquid composition -- 100 -- a weight section -- receiving -- a phenolic antioxidant -- (- C --) -- 0.1 - five -- a weight section -- Lynn -- a system -- an antioxidant -- (- D --) -- 0.01 - five -- a weight section -- and -- an ultraviolet ray absorbent -- and/or -- a hindered amine light stabiliser -- (- E --) -- 0.5 - ten -- a weight section -- containing -- hardenability -- a constituent -- it is . Below, this invention is explained in full detail.

[0008]A hardenability constituent of this invention makes indispensable a liquid composition whose polymerization nature monomer (A) is 40 to 100 % of the weight and a polymer and/or whose oligomer (B) are 0 to 60 % of the weight. The above-mentioned weight percentage is the value which made total weight with a polymerization nature monomer (A), a polymer, and/or oligomer (B) 100 % of the weight. When the above-mentioned polymerization nature monomer (A) makes the whole quantity 100 % of the weight, acryloyl ester which has a hydroxyl group (meta) is 25 to 80 % of the weight. As for the above-mentioned polymerization nature monomer (A), when the whole quantity is made into 100 % of the weight, it is preferred that acryloyl ester (meta) is 80 to 100 % of the weight. That is, it will be set up some or all in it serve as acryloyl ester which has a hydroxyl group (meta), and become in a mentioned range although it is preferred that acryloyl ester (meta) is 80 to 100 % of the weight among 100 % of the weight of polymerization nature monomers (A).

[0009]A weight percentage of acryloyl ester which has the above-mentioned hydroxyl group as a more desirable gestalt of this invention about the above-mentioned weight percentage (meta) is 30 to 60 % of the weight. It is 35 to 50 % of the weight preferably. A weight percentage of the above-mentioned (meta) acryloyl ester is 90 to 100 % of the weight. A weight percentage of the above-mentioned polymer and/or oligomer (B) is 1 to 60 % of the weight. It is 5 to 50 % of the weight, and is 5 to 40 % of the weight most preferably. When it separates from these ranges, there is a possibility that it may become impossible to demonstrate a operation effect which each component has.

[0010]In the above-mentioned liquid composition, as for acryloyl ester which has a hydroxyl group (meta), heat-resistant coloring nature, substrate adhesion, etc. are mentioned as a operation effect which each component has, for example, Intensity, substrate adhesion, pliability, etc. will be mentioned and acryloyl ester (meta) will demonstrate these operation effects with sufficient balance. Intensity, toughness, transparency (compatibility), etc. are mentioned in what introduced a double bond into a side chain so that low shrinkage nature at the time of hardening, etc. might be mentioned and a polymer and/or oligomer (B) might be mentioned later. As for a polymer and/or oligomer (B), in order to fully demonstrate such a operation effect, it is preferred that it is meltable to a

polymerization nature monomer (A).

[0011]One sort, such as what it is not limited especially as the above-mentioned (meta-) acrylic ester, for example, is mentioned to the following (1) - (5), -- or two or more sorts can be used.

(1) (meta) Acrylic ester: Methyl (meta) acrylate, Ethyl (meta) acrylate, n-propyl (meta) acrylate, n-butyl (meta) acrylate, i-butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, lauryl (meta) acrylate, Cyclohexyl (meta) acrylate, glycidyl (meta) acrylate, Methoxy ethylene glycol (meta) acrylate, ethoxyethylene glycol (meta) acrylate, Methoxy diethylene-glycol (meta) acrylate, ethoxydiethylene-glycol (meta) acrylate, Methoxy propylene glycol (meta) acrylate, methoxy polyethylene-glycol (meta) acrylate, Ethoxypolyethylene-glycol (meta) acrylate, allyl (meta) acrylate, acrylate (meta) of an oligo ethyleneoxide addition of allyl alcohol, acrylate (meta) of a polypropylene oxide addition of allyl alcohol, etc.

[0012](2) Basic (meta) acrylate : dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, etc.

(3) (meta) Acrylamide: (meta) Acrylamide etc.

[0013]The acrylate which has a hydroxyl group (meta) : (4) 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 3-hydroxybutyl (meta) acrylate, Methyl 2-(hydroxymethyl) acrylate, ethyl 2-(hydroxymethyl) acrylate; Polyethylene-glycol mono- (meta) acrylate, The mono- (meta) acrylate of polyhydric alcohol which has two hydroxyl groups, such as polypropylene-glycol mono- (meta) acrylate; Di(meth)acrylate of tris(hydroxyethyl) isocyanuric acid, The partial (meta) acrylate of polyhydric alcohol which have three or more hydroxyl groups, such as penta ERIS RITORURI (meta) acrylate

[0014](5) Other acrylic (meta) monomers; (meta) acrylonitrile, an acrolein (meta), etc.

Also in these, it is preferred to use methyl methacrylate from points, such as compatibility and intensity of a hardened material.

[0015]If pliability is given and it excels in order to use a hardenability constituent of this invention for uses, such as a shock buffer, an elastic buffer of a substrate, a sealing agent, adhesives, encapsulant, an inclusion agent, substrate protection, and a destructive preventing scattering agent of a substrate, it is preferred that Tg of a homopolymer, for example, uses a low polymerization nature monomer (A). Specifically Methyl acrylate, ethyl acrylate, acrylic acid isopropyl, acrylic acid n-butyl, acrylic acid n-heptyl, Acrylic acid pentyl, acrylic acid benzyl, acrylic acid hexyl, acrylic acid heptyl, Acrylic acid 2-octyl, 2-ethylhexyl acrylate, acrylic acid cyclohexyl, Acrylic acid octyl, acrylic acid 2-octyl, acrylic acid nonyl, Acrylic acid dodecyl, acrylic acid 2-methoxy ethyl, n-butyl methacrylate, It is preferred to use methacrylic acid i-butyl, methacrylic acid pentyl, methacrylic acid hexyl, 2-ethylhexyl methacrylate, methacrylic acid octyl, methacrylic acid dodecyl, methacrylic acid tetradecyl, methacrylic acid hexadecyl, methacrylic acid octadecyl, etc.

[0016]As the above-mentioned polymerization nature monomer (A), this and a copolymerizable polymerization nature monomer can also be used in addition to acrylic ester (meta), one sort, such as what is specifically listed to below, -- or two or more sorts can be used. (Meta) Acrylamide; (meta) Acrylonitrile, acroleins (meta); styrene, Vinyl ester, such as styrene; vinyl acetate, such as alpha-methylstyrene, vinyltoluene, and chlorostyrene; The methyl vinyl ether, Vinyl ether, such as ethyl vinyl ether and butylvinyl ether; Allyl alcohol, N-substitution maleimide, such as allyl compound; N-phenylmaleimide, such as allyl glycidyl ether, ethylene glycol monoallyl ether, and propylene glycol monoallyl ether, N-cyclohexylmaleimide, and N-isopropylmaleimide

[0017]Especially if it is a range which does not have a operation effect of this invention checked as a weight percentage of the above-mentioned (meta) acrylic ester and a copolymerizable polymerization nature monomer, it will not be limited, but it is preferred that it is 20 or less % of the weight in 100 % of the weight of polymerization nature monomers (A). It is 10 or less % of the weight more preferably. [0018]It is not limited especially as acrylic ester which has the above-mentioned hydroxyl group (meta). For example, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 3-chloro-2-hydroxyethyl (meta) acrylate, 3-hydroxyethyl (meta) acrylate, etc. are mentioned. These may be used independently and may use two or more sorts together. If pliability is given to a hardened material and it excels in it also in these, it is preferred to use 2-hydroxyethyl acrylate and 2-hydroxypropyl acrylate from balance of intensity and pliability.

[0019]what it is not limited especially as a polymer in this invention, and/or oligomer (B), for example, is mentioned to the following (1) - (4) -- one sort -- or two or more sorts can be used.

(1) Methyl (meta) acrylate, ethyl (meta) acrylate, Propyl (meta) acrylate, n-butyl (meta) acrylate, t-butyl (meta) acrylate, isobutyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, n-nonyl (meta) acrylate, Decyl (meta) acrylate, cyclohexyl (meta) acrylate, Benzyl (meta) acrylate, dicyclopentyl(metha) acrylate, JISHIKURO pentenyl (meta) acrylate, 2-JISHIKUROPENTENOKISHI. ethyl (meta) acrylate, Isobornyl (meta) acrylate, methoxy ethyl (meta) acrylate, Ethoxyethyl (meta) acrylate, butoxyethyl (meta) acrylate, Methoxy ethoxyethyl (meta) acrylate, ethoxyethoxyethyl (meta) acrylate, Tetrahydrofurfuryl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 1 functionality (meta) acrylate monomers, such as 2-hydroxypropyl (meta) acrylate, 4-hydroxybutyl (meta) acrylate, acrylic acid (meta), and acryloyl morpholine (meta), etc. Acrylonitrile, vinyl acetate vinyl propionate, butadiene, styrene, A homopolymer or a copolymer of acrylate monomers, such as ethylene (meta), and a copolymerizable monomer, cellulose type polymers; diallyl-phthalate-resin; EPOSHIKI resin;

VCM/PVC, such as cellulose acetate butyrate and cellulose acetate propionate, vinyl acetate resin.

[0020](2) A monomer which has a functional group for making an acrylyl group or a methacryloyl group introduce into at least one sort and a side chain of the above-mentioned (meta) acrylate monomer, or this and a copolymerizable monomer. For example, a maleic anhydride, acrylic acid, methacrylic acid, 2-hydroxyethyl acrylate, A polymer produced by making at least one sort of monomers chosen from 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, and 2-hydroxypropyl methacrylate react.

[0021](3) the bottom of existence of a copolymer of the above (2) -- (a)2-hydroxyethyl (meta-) acrylate. Alcohols which have acrylyl groups (meta), such as 2-hydroxypropyl (meta) acrylate, (b) An epoxy compound which has acrylyl groups (meta), such as glycidyl (meta) acrylate, (c) An addition of tolylene diisocyanate and 2-hydroxypropyl methacrylate, A polymer which has an acrylyl group or a methacryloyl group in a side chain produced by making an unsaturation isocyanate compound etc. which have an acrylyl group (meta) and isocyanate groups of isophorone diisocyanate and hydroxyethyl acrylate, such as an addition, react.

[0022](4) Polybasic acid and ethylene glycol, such as phthalic acid and adipic acid, Polyhydric alcohol, such as butanediol, (Meta) Polyester poly obtained at a reaction of acrylic acid. (Meta) Acrylate; An epoxy resin. (Meta) Epoxy poly (meta) acrylate obtained at a reaction with acrylic acid oligomer, such as urethane poly (meta) acrylate obtained at a reaction of polyol, polyisocyanate, and hydroxyl group content monomers, such as 2-hydroxyethyl (meta) acrylate.

[0023]Also in these, it is preferred to use an acrylic (**) polymer from a point of the weatherability of a hardened material or low coloring nature (transparency). It is using more preferably a polymer which has two or more polymerization nature double bonds in intramolecular from intensity of a hardened material, balance of pliability, or a point of compatibility. Although indicated in detail to Japanese Patent Application No. 11-171518 as a concrete manufacturing method of a polymer which has two or more polymerization nature double bonds in intramolecular, For example, copolymerization of methacrylic acid ester and methacrylic acid, such as methyl methacrylate, is carried out, and a method of adding glycidyl methacrylate to carboxylic acid in a polymer after an end of a polymerization, etc. are mentioned.

[0024]this invention -- hardenability -- a constituent -- the above -- a liquid composition -- 100 -- a weight section -- receiving -- a phenolic antioxidant -- (- C --) -- 0.1 - five -- a weight section -- Linn -- a system -- an antioxidant -- (- D --) -- 0.01 - five -- a weight section -- and -- an ultraviolet ray absorbent -- and/or -- a hindered amine light stabiliser -- (- E --) -- 0.5 - ten -- a weight section -- containing .

[0025]It is making content of the above-mentioned phenolic antioxidant (C) into 0.2 - 3 weight section as a more desirable gestalt of this invention about the above-mentioned weight percentage. They are 0.5 - the amount part of duplex more preferably. It is making content of the above-mentioned Linn system antioxidant (D) into 0.02 - 3 weight section. They are 0.05 - the amount part of duplex more preferably. It is making content of the above-mentioned UV absorbent and/or a hindered amine light stabiliser (E) into 0.5 - 6 weight section. It is 0.5 to 4 weight section more preferably. As ratio C/D of the above-mentioned phenolic antioxidant (C) and the above-mentioned Linn system antioxidant (D), 20 from a point / 1 - 1/10 of coloring at a time of making it harden are preferred. More preferably, it is 20 / 1 - 2/1, and is 10 / 1 - 5/1 still more preferably. When it separates from these ranges, there is a possibility that it may become impossible to demonstrate a operation effect which each component has. As a operation effect which each above-mentioned

component has, heat-resistant coloring nature, weatherability (light) nature, etc. are mentioned, for example.

[0020]It is not limited especially as the above-mentioned phenolic antioxidant (G). For example, Sumi Reiser GM, Sumi Reiser GS, Sumi Reiser BHT, SUMIRAIZAS, Sumi Reiser GA-80, and Sumi Reiser WX-R (any — a trade name.); by Sumitomo Chemical Co., Ltd. — ADEKA sub AO-20 and ADEKA sub AO-30, ADEKA sub AO-40, ADEKA sub AO-50, ADEKA sub AO-60, and ADEKA sub AO-70 — it ADEKA-sub-AO—330(all are a trade name and the Asahi Denka Kogyo [K.K.]—make)—; ANTEJ-DBH(ing), and, ANTEJ DAH, ANTEJ W-400, ANTEJ W-500 (all are a trade name and the Kawaguchi Chemical Industry Co., Ltd. make), etc. are mentioned. These may be used independently and may use two or more sorts together. Also in these, it is preferred to use Sumi Reiser GA-80 from points, such as a synergistic effect with coloring nature and the Linn system antioxidant.

[0021]It is not limited especially as the above-mentioned Linn system antioxidant (D), but For example, ADEKA sub PEP-40, ADEKA sub PEP-8, ADEKA sub PEP-11C, ADEKA sub PEP-24G, ADEKA sub PEP-36, ADEKA sub HP-10, the ADEKA sub 2112, the ADEKA sub 260, the ADEKA sub 522A, The ADEKA sub 329K, the ADEKA sub 1178, the ADEKA sub 1500, the ADEKA sub G, the ADEKA sub 135A, the ADEKA sub 3010, the ADEKA sub TPP (all are a trade name and the Asahi Denka Kogyo K.K. make), etc. are mentioned. These may be used independently and may use two or more sorts together. Also in these, it is preferred to use the ADEKA sub 1500 from points, such as a synergistic effect with coloring nature and a phenolic antioxidant.

[0022]It is not limited especially as the above-mentioned UV absorber, but For example, the tinuvin P, the tinuvin 234, the tinuvin 326, the tinuvin 327, the tinuvin 328, the tinuvin 213, the tinuvin 320, the tinuvin 384, the tinuvin 400, the tinuvin 900, the tinuvin 928, and the tinuvin 1130 (any — a trade name.) Ciba Specialty Chemicals; — RUVA-93 (a trade name), The Otsuka Chemical Co., Ltd. make, SEESORB102, SEESORB105, SEESORB201, SEESORB202, SEESORB501, SEESORB502, SEESORB708 (all are a trade name and the SHIPRO KASEI KAISHA, LTD. make), etc. are mentioned. These may be used independently and may use two or more sorts together. Also in these, it is preferred to use the tinuvin 320, the tinuvin 1130, SEESORB202, and RUVA-93 from points, such as initial coloring and UV absorbance. It is RUVA-93 from a point of bleeding-proof nature more preferably.

[0023]It is not limited especially as the above-mentioned hindered amine light stabiliser. For example, ADEKA sub LA-52, ADEKA sub LA-57, ADEKA sub LA-62, ADEKA sub LA-67, ADEKA sub LA-63P, ADEKA sub LA-68LD, ADEKA sub LA-77, ADEKA sub LA-82, and ADEKA sub LA-87 (any — a trade name.) Asahi Denka Kogyo K.K. make; tinuvin 111FD, the tinuvin 144, the tinuvin 123, the tinuvin 292 (above made in Tiba Specialty Chemicals), etc. are mentioned. These may be used independently and may use two or more sorts together. Also in these, it is preferred to use ADEKA sub LA-82 and ADEKA sub LA-87 from a point of bleeding-proof nature.

[0030]Other than above-mentioned (A) — (E), a hardenability constituent of this invention may

contain one sort of other components, such as polyfunctional monomer (F), acrylic acid (meta) (G), a

coupling agent (H), and plasticizer (I), or two sorts or more, and does not need to contain them. By

being able to raise more intensity, toughness, and transparency (compatibility) of a hardened material,

and including acrylic acid (meta) (G) and a coupling agent (H) by including polyfunctional monomer (F),

Shrinkage characteristics at the time of hardening are more improvable by being able to raise

substrate adhesion more and including plasticizer (I).

[0031]It is preferred to make content of polyfunctional monomer (F) into 0 — 10 weight section to the

liquid composition 100 above-mentioned weight section as content of the above (F) — (I). It is 0.1 to 3

weight section more preferably. It is preferred to make content of acrylic acid (meta) (G) into 0 — 10

weight section. More preferably, it is 0.5 to 5 weight section, and they are 1 — the amount part of

diplexes still more preferably. It is preferred to make content of a coupling agent (H) into 0 — 10

weight section. More preferably, it is 0.5 to 6 weight section, and is one to 3 weight section still more

preferably. And it is preferred to make content of plasticizer (I) into zero to 50 weight section. More

preferably, it is zero to 30 weight section, and is zero to 20 weight section still more preferably. When

it separates from these ranges, there is a possibility that it may become impossible to demonstrate a

operation effect which each component has.

[0032]It is not limited especially as the above-mentioned polyfunctional monomer (F), but For

example, ethylene glycol di(meth)acrylate, 1, 4-butanediol di(meth)acrylate, 1,6-hexanediol di

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(meth)acrylate, Neopentyl glycol di(meth)acrylate, diethylene GURIKORUJI (meta) acrylate, Triethylene glycol dimethacrylate, TORIMECHI roll pro pantry (meta) acrylate, Multivalent ester of methacrylic acid, such as Venter Elisit Tori (meta) acrylate, Venter Elisit tetra (meta) acrylate, or glycerin dimethacrylate, or acrylic acid, and polyhydric alcohol is mentioned. These may be used independently and may use two or more sorts together. Also in these, it is preferred to use triethylene glycol dimethacrylate.

[0033]As the above-mentioned (meta) acrylic acid (G), any one sort of acrylic acid and methacrylic acid may be used, and these two sorts may be used together. It is preferred to use acrylic acid from balance of intensity and pliability.

[0034]It is not limited especially as the above-mentioned coupling agent (H), for example, vinyl-tris-(beta-methoxyethoxy) Silang, gamma-methacryloxypropyl trimethoxy silane, gamma-mercaptopropyltrimethoxysilane, gamma-aminopropyl triethoxysilane, etc. are mentioned. An organic metal system bonding assistant can be used like a coupling agent (H), and it is not limited especially as such an organic metal system bonding assistant, for example, tetraisopropyl titanate, tetrabutyl titanate, etc. are mentioned. These may be used independently and may use two or more sorts together. Also in these, when a substrate is glass, it is preferred to use a silane coupling agent from an adhesive point, and, specifically, it is preferred to use gamma-methacryloxypropyl trimethoxy silane.

[0035]It is not limited especially as the above-mentioned plasticizer (I), for example, they are

mentioned by ester of phthalic acid, adipic acid, sebacic acid or citrate, and alkanol, etc., and

specifically, Dimethyl phthalate, dibutyl phthalate, dioctyl phthalate, dioctyl horse mackerel pinnate,

dioctyl SEBASHINETO, acetyl tributyl citrate, etc. are mentioned. These may be used independently

and may use two or more sorts together. Also in these, it is preferred to use acetyl tributyl

SHTONETO from a heat-resistant point.

[0036]A hardenability constituent of this invention is not limited especially as the preparing method,

although it can obtain by mixing each component mentioned above. For example, when adding a liquid

composition which makes indispensable a polymerization nature monomer (A), a polymer, and/or

oligomer (B) and mixing, it adds, after preparing a mixture of (A) and (B), and a hardenability

constituent may be produced, (A) and (B) may be added independently, and a hardenability

constituent may be produced.

[0037]It is not limited especially as curing conditions of a hardenability constituent of this invention,

but all of a curing method currently performed from the former can be used. For example, a pyrolysis

polymerization initiator like organic peroxide or an azo compound may be used as a hardening agent,

and lights, such as ultraviolet rays (UV) and visible light, may be irradiated with and stiffened using

photopolymerization initiators, such as a benzoyl system, a phosphine system, and a metalloene

system, etc. Hardening accelerators, such as metal salt and amines, may be used together. It is

preferred to carry out heat cure from a point of coloring, also in these, using a pyrolysis

polymerization initiator without using an accelerator.

[0038]As for curing temperature, as a desirable gestalt of the above-mentioned curing conditions, it

is preferred to consider it as not less than 40 **, for example. There is a possibility that a hardened

material of low coloring may become selection of a curing system which becomes being less than 40

** with low coloring is difficult, and is hard to be obtained as a result. It is 50-100 ** more preferably.

In a curing system of an inside low temperature service, when sufficient hardening is it hard to be

obtained to be less than 50 ** and it exceeds 100 **, there is a possibility that cost and a running

cost of curing oven which can harden a large-sized article may become great. 60-80 ** comes out

preferably. It is preferred to perform not less than 80 ** posture.

[0039]As a desirable hardening agent in a case of hardening during the above with curing temperature

of 50-100 ** of a low temperature service, organic peroxide 70 ** or less is mentioned for 10 hour

half life period temperature, for example. Thereby, it becomes possible to raise more the

characteristics, such as inside cold cure nature, low coloring nature, heat-resistant coloring nature,

and weatherability (light) nature. Specifically, it is preferred to use diacyl peroxide, peroxy dicarbonate,

and peroxy ester species. Specifically Cumil peroxy neodecanoate, diisopropyl peroxy dicarbonate, 1,

1, 3, and 3-tetramethyl butylperoxyneodecanoate, Bis(4-t-butylcyclohexyl)peroxy dicarbonate, t-

hexylperoxy neodecanoate, t-butylperoxy neodecanoate, lauroyl peroxide, 1, 1 and 3, and 3-

tetramethyl butylperoxy 2-ethylhexanoate etc. are mentioned. It is good to use more preferably a

http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web.cgi?atw_u=http%3A%2F%2Fwww4.ipdl.i...

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hardening agent whose 10 hour half life period temperature is 40-85 °C from a point of hardenability and an ease of handling.

[0040]As a compound of others which can be blended with a hardenability constituent of this invention, although based on the purpose of use, it is a range on which transparency is not dropped, and colorant, thermal polymerization inhibitor, a leveling agent, a surface-active agent, a defoaming agent, preservation stabilizer, lubricant, a solvent, a filler, aggregate, an antiaging agent, a wettable improving agent, a low profile additive, an internal release agent, paraffin, etc. are mentioned, and these one sort or two sorts or more may be included, for example.

[0041] [Example]Although an example is lifted to below and this invention is explained to it still in detail, this invention is not limited only to these examples. Among an example, especially, a "part" means a "weight section", as long as there is no notice.

[0042]Synthetic example 1 97.2 copies of methyl methacrylate and 2.8 copies of methacrylic acid were taught to the synthesizing temperature meter of meta-acryl syrup (1), the condenser tube, the gas introducing pipe, and the reactor provided with the agitator, and nitrogen gas replaced the inside of a reactor with them. Stirring this mixture, carry out temperature up to 80 °C, and Next, 0.008 copy of azobisisobutyronitrile. After adding 0.6 copy of n-dodecyl mercaptan and performing a copolymerization reaction for 4 hours, while blowing air into the system, the ANTEJI W-400 (trade name, Kawaguchi Chemical Industry Co., Ltd. make) 0.06 copy was added, and the polymerization was suspended.

[0043]Subsequently, after adding 3.2 copies of metaglycidyl acrylate, and 0.2 copy of tetraphenyl phosphonium bromide to contents, temperature up was carried out to 90 °C, and it reacted under an air atmosphere for 6 hours, and target meta-acryl syrup was obtained. In the weight average molecular weight of polystyrene conversion of the solid content according [solids concentration] to 33% and gel permeation chromatography, 71000 and viscosity 2300 mPa·s. The polymerization nature double bond equivalent (weight average molecular weight per double bond of a polymer) by which the Haasen color number is contained in 0 and a polymer was 11100. The obtained meta-acryl syrup was used as meta-acryl syrup (1).

[0044]A resin composition (hardenability constituent) is blended of the ingredient shown in one to Examples 1-7 and comparative example 5 Table 1 and 2. It was made to harden by the thickness of 1-mm thickness between two 3-mm thickness float sheet glass (JIS-R3202) according to the curing conditions of (however, the number in front is a weight section), shown (**), or (***), and the specimen was obtained. Various examinations were done about this specimen and that result was shown in Table 3 and 4.

[0045]

[Table 1]

	実施例									
	1	2	3	4	5	6	7			
硬化剤	30	40	40	—	—	—	—			
HA	—	—	—	40	40	40	40			
メチルメタクリレート	54.45	—	—	—	—	—	—			
ブチルメタクリレート	—	29.45	29.45	29.45	19.45	29.55	9.45			
メタクリルナフタレン(1)	—	25	25	25	35	25	45			
GA-80	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
アデカスタブ1500	0.05	0.05	0.05	0.05	0.05	0.05	0.05			
LA-82	0.5	0.5	0.5	0.5	0.5	—	0.5			
RUVA-93	0.5	0.5	0.5	0.5	0.5	0.5	0.5			
3EG	10	—	—	—	—	—	—			
アクリル酸	2	2	2	2	2	2	2			
A-174	2	2	2	2	2	2	2			
パーヘキシルND	0.5	—	—	—	—	—	—			
パーヘキシルND	—	1	—	1	1	1	1			
パーヘキシルND	—	—	—	—	—	—	—			
パーヘキシルND	0.5	—	—	—	—	—	—			
パーヘキシルND	0.5	—	—	—	—	—	—			
硬化条件	(9)	(7)	(4)	(4)	(4)	(4)	(4)			

[Table 2]

	比較例									
	1	2	3	4	5					
HA	30	40	40	40	40					
メチルメタクリレート	49.45	29.94	29.499	30	30.25					
GA-80	0.5	0.01	0.5	—	0.5					
アデカスタブ1500	0.05	0.05	0.001	—	0.05					
LA-82	0.5	0.5	0.5	0.5	0.1					
RUVA-93	0.5	0.5	0.5	0.5	0.1					
メタクリルナフタレン(1)	25	25	25	25	25					
アクリル酸	2	2	2	2	2					
A-174	2	2	2	2	2					
パーヘキシルND	1	1	1	1	1					
パーヘキシルND	—	—	—	—	—					
パーヘキシルND	—	—	—	—	—					
硬化条件	(4)	(4)	(4)	(4)	(4)					

[0047]Table 1 and 2 is explained below. In the presentation of a hardenability constituent. HEA is hydroxyethyl acrylate and with HPA. Are hydroxypropyl acrylate and with GA-80. Are antioxidant Sumi Reiser GA-80 (a trade name, the Sumitomo Chemical Co., Ltd. make), and in the ADEKA stub 1500 (trade name). Are a phosphite system antioxidant by Asahi Denka Kogyo K.K., and with LA-82. Are light stabilizer ADEKA stub LA-82 (a trade name, the Asahi Denka Kogyo K.K. make), and with RUVA-93 (trade name). Are an ultraviolet ray absorbent by Otsuka Chemical Co., Ltd., and with 3EG. Are triethylene glycol dimethacrylate and in A-174 (trade name). It is the Nippon Unicar silane coupling agent, and is a hardening agent by Nippon Oil & Fats Co., Ltd. in par oil TCP, par hexyl ND, par oil LO, the par octa O, and the par hexa TMH (all are trade names). On curing conditions, curing-conditions (a) is 60 °C 1 hour. Curing-conditions (b) is 80 °C 1 hour, and curing-conditions (c) is 130 °C 10 minutes.

[0048]It is as [test methods / in an example and a comparative example / various] follows. [Hardenability] The hardenability at the time of making it harden in each curing conditions was evaluated.

O : hardening

x: Unhardened.

[0049][Substrate adhesive property] After repeating +(20 °C 18 hours) (-20 °C 3 hours)+ (50 °C 3 hours) for the adhesive property over a substrate as a cycle based on a JIS-A6909 hot-cold cyclic test, viewing estimated appearance.

O : separation is not seen at all.

** : Separation is seen a little.

x: Many separation is seen.

[0050][Tensile strength and *** pace of expansion] The casting board of 3-mm thickness was produced to the examination. According to the tensile test of JIS-K6301, as for 1/2 size of the No. dumbbell-like 2 type [specimen], and specimen grip distance, the movement speed of 20 mm and a specimen grip examined by a part for 100-mm/.

[0051][Visible light transmittance] Early transparency was measured with the visible-light-transmittance plan (the Nippon Denshoku Industries make, trade name "sigma90 system"). [0052][Low coloring nature] The yellow index [in / for early low coloring nature / with a visible-light-transmittance meter (the Nippon Denshoku Industries make, trade name "sigma90 system") / transparent mode] (YI) was measured.

[0053][Elevated-temperature coloring nature] Color difference (deltaE) with the first stage [in / for the coloring nature after being exposed in 120 °C for 1000 hours / with a visible-light-transmittance meter (the Nippon Denshoku Industries make, trade name "sigma90 system") / transparent mode] was measured.

[0054][Weatherability] Viewing estimated the coloring nature after being exposed outdoors for a long period of time.

O : coloring is not seen at all.

** : Coloring is seen a little.

x : Coloring is seen considerably.

[0055]

[Table 3]

	実施例						
	1	2	3	4	5	6	7
硬化性	O	O	O	O	O	O	O
基材密着性	Δ	Δ	Δ	O	Δ	O	Δ
引張強度 (MPa)	5.0	0.34	0.34	0.60	1.2	0.6	2.4
引張伸び率 (%)	120	100	100	150	140	150	50
可塑性透過率 (%)	89	89	89	89	89	89	89
低着色性 (YI)	0.26	0.36	0.36	0.06	0.26	0.12	0.28
高温着色性 (ΔE)	0.49	0.43	0.43	0.48	0.58	0.63	0.95
屋外着色性	O	O	O	O	O	O	O

[0056]

[Table 4]

	実施例				
	1	2	3	4	5
硬化性	O	O	O	O	O
基材密着性	Δ	O	O	O	O
引張強度 (MPa)	0.29	0.60	0.60	0.60	0.60
引張伸び率 (%)	70	150	150	150	150
可塑性透過率 (%)	89	89	89	89	89
低着色性 (YI)	0.10	0.31	0.10	0.10	0.18
高温着色性 (ΔE)	3.50	1.31	1.24	1.72	1.21
屋外着色性	Δ	Δ	Δ	Δ	x

[0057]Table 3 showed that it had each hardened material formed from the hardenability constituent produced in Examples 1-7, and good physical properties could be used for it good. The hardened material formed from the hardenability constituent produced by the comparative examples 1-5 is inferior to physical properties, such as weatherability, compared with what was produced in Examples 1-7

[0058]

[Effect of the Invention]Since the hardenability constituent of this invention consists of above-mentioned composition, it excels in transparency or low coloring nature. And it is possible to form the hardened material which can maintain transparency and low coloring nature after elevated-temperature exposure or extended outdoor exposure over a long period of time, and also transparency and low coloring nature have been maintained. It is possible to realize inside cold cure nature, and transparency and low coloring nature have been maintained. From it being possible to make good balance of a substrate adhesive property, substrate adhesion, elastic repeatability, and the *** pace of expansion of tensile strength. For example, it can use conveniently in fields, such as mold goods, a laminated piece, a cast article, a shock buffer, the elastic buffer of a substrate, a sealing agent, adhesives, encapsulant, an inclusion agent, substrate protection, and a destructive preventing scattering agent of a substrate.

[Translation done.]